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A STUDY OF AZOXY COMPOUNDS

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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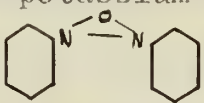
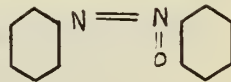
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A STUDY OF AZOXY COMPOUNDS.

Introduction.

It was pointed out in 1902 by Meyer and Jacobson¹ that our knowledge of azoxy compounds is very incomplete and that the formula $R-\text{N}=\text{N}-R$ explains reactions just as well as the commonly accepted $R-\text{N}(\text{O})-\text{N}-R$ formula. If the formula $R-\text{N}(\text{O})-\text{N}-R$ is the correct one, isomeric compounds should be obtained in the preparation of unsymmetric azoxy compounds. The present work has been undertaken to throw additional light on this subject by preparing unsymmetric azoxy compounds and thereby investigating the possibility of formation of isomeric forms.

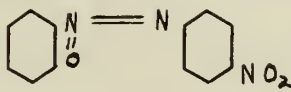
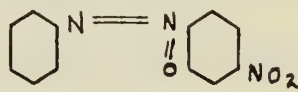
Historical Part.

Azoxy compounds have been known for a long time. In 1845 Zinin² prepared azoxy benzene by the action of potassium hydroxide on nitro benzene. He assigned the formula  which has been generally accepted although there have always been some chemists who did not agree to it, since the formula  would explain the reactions of the compound equally well. Recent work, however, seems to point to the latter formula as the correct one.

Considerable work has been done upon isomeric compounds. In 1889, Janovsky and Reimann³ claimed to have prepared isomeric azoxytoluenes by the action of zinc dust and soda on p-nitro tol-


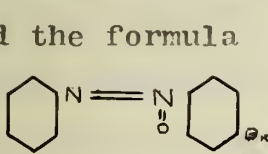
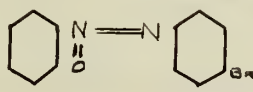
uene. The two isomeric azoxy compounds melted at 75° and 70° respectively. Klinger and Zuurdeeg⁴, however, in the next year showed that one of the isomeric compounds consisted of a mixture.

In 1909 again, Reissert⁵ stated that he prepared some isomeric azoxy compounds. By treating nitroso benzene at a low temperature with aqueous alcoholic sodium hydroxide, he obtained the known azoxy benzene and also a small quantity of iso azoxy benzene which melted at 84° . Similarly, o-nitrosotoluene yielded o-azoxy toluene and o-isoazoxytoluene which melted at 82° , the latter product forming the main product. The iso compounds pass into the isomeric compound when heated.

By far, the greatest and most important work has been done by Angelo Angeli and his co-workers. In 1910, he⁶ first prepared azoxybenzene by the oxidation of azobenzene with hydrogen peroxide in glacial acetic acid solution. He did not obtain the isomers described by Reissert. In 1911, Angeli and Alessandri⁷ prepared p-nitro azoxy benzene by oxidizing p-nitro azobenzene with hydrogen peroxide. They obtained a compound melting at 148° , differing in color and solubilities from the p-nitro azoxybenzene prepared by Zinin⁸ from nitrosobenzene and p-nitroaniline which melted at 152° . They suggested that the two substances are isomerides having the formulas  and  respectively.

Neither Zinin's nitro-azoxybenzene nor its proposed isomer⁹ react with bromine in acetic acid, but if mixed with a little iodine and then added to bromine, Zinin's compound is not acted upon but its isomer yields a bromo derivative, crystallizing in

yellow prisms which melt at 199° . Azoxybenzene made under similar conditions gives a bromo derivative which melts at 73° .

Angeli and Valori¹⁰, working with the bromo derivatives, prepared p-bromoazoxybenzene by oxidizing p-bromoazobenzene with hydrogen peroxide. They obtained the α -p-bromoazoxybenzene, yellow crystals melting at 73° , which was identical with the compound mentioned above, and also β -p-bromoazoxybenzene, yellow crystals melting at 92° . These compounds could not be converted into each other, but each gave p-bromoazobenzene on reduction with aluminum amalgam. The α -p-bromoazoxybenzene was not reacted on by the bromine but the β -p-bromoazoxybenzene when treated with bromine gives 4:4'-dibromazoxybenzene. This shows that a bromine atom enters in the para position into each $=N$  residue, a dibromide $=NC_6H_3Br_2$ being probably first formed and then decomposed in $=N.C_6H_4Br$ and HBr . This reaction makes it possible to determine the constitution of isomeric azoxy compounds. They assigned the formula  to the α compound and  to the β compound. Angeli and Valori¹¹ also prepared isomeric azoxybenzene

carboxylic acids.

Angeli¹² in 1914 prepared an azoxy phenol containing only one hydroxyl group. He protected this group by acetylation while he oxidized the azo compound with hydrogen peroxide. The α compound, melting at 148° , was obtained. This was found to be a mixture of the isomeric derivatives, the β form melting at 107° and the α form at 156° . The ethyl ethers of these two compounds were made, the α form melting at 72° and the β form melting

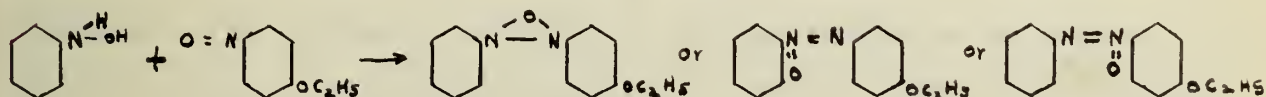
at 55°. Both of these azoxy ethers can be reduced to the same azo ether showing them to be true isomers.

Gatterman and Ritschke¹³ in 1890 prepared small quantities of 4-4' anisol azoxyphenetol by reducing p-nitro anisol with sodium in ethyl alcohol solution. In 1904 Rising¹⁴ prepared the 4-4' anisol azoxy phenetol from p-phenetol-hydroxyl-amine and p-nitroso-anisol. In neither instance was the formation of isomeric compounds reported.

Theoretical Part.

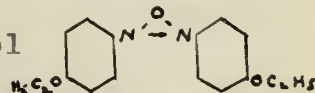
Angeli⁶, by his oxidation of azo compounds with hydrogen peroxide in glacial acetic acid solution claimed to have prepared isomeric azoxy compounds differing in their physical and chemical properties and having the formulae $R-\overset{\overset{O}{\parallel}}{N}-N-R'$ and $R-\overset{\overset{O}{\parallel}}{N}-N-R'$ respectively.

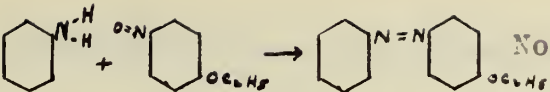
In the present work, attempts were made to prepare unsymmetric azoxy compounds by other methods and to isolate and study any isomers obtained. Phenyl-hydroxyl-amine was treated with p-nitroso-phenetol with and without a solvent.



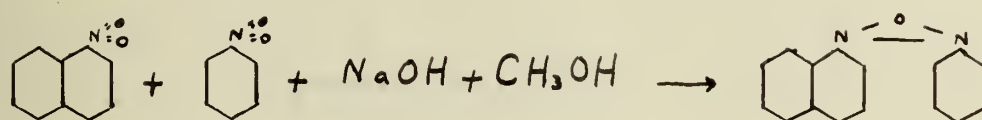
This reaction did not occur however and instead two molecules of p-nitroso-phenetol united to form azoxy-phenetol both in the presence of a solvent and also when fused

together without a solvent. Molecular amounts of aniline and p-nitroso-phenetol were mixed together in order to prepare an un-



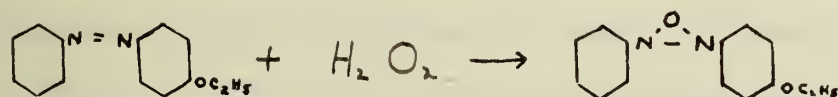
symmetrical azo compound  No reaction occurred and the two substances separated as an oil when poured into water.

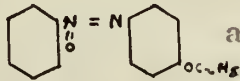
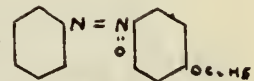
Phenyl-azoxynaphthalene was prepared by the reduction of α -nitronaphthalene and nitro-benzene with sodium hydroxide in methyl alcohol solution.



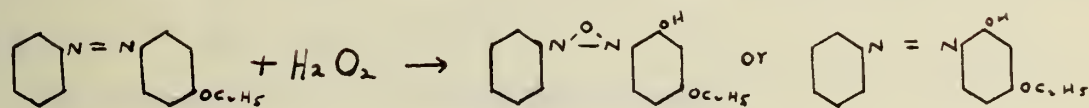
No isomers were observed, possibly because only a small amount of product was obtained. The crystals were light brown, melting at 67.5° .

The ethyl ether of azoxy-benzene was prepared by the oxidation of ethoxyazo-benzene with hydrogen peroxide in glacial acetic solution.



According to Angeli, the isomers  and  with melting points at 72° and 55° respectively, should have been obtained. The compound melting at 55° was isolated as yellow, leaf-like crystals. A substance melting at 69° - 70° was also obtained. A combustion showed this to be mainly ethoxyazobenzene probably mixed with a little of the azoxy compound. No other indications of an isomeric azoxy-compound were observed. There was, however, a very small amount of a phenolic compound formed which melted in an impure state at 57° - 60° . These crystals were brown. This phenol may have been the product of a further oxidation of the ethoxy-

azoxy benzene or of the ethoxyazobenzene, the oxygen atom having combined with the carbon in the ring instead of with the nitrogen.



Experimental Part.

I.

A. - Attempts to Prepare Unsymmetrical Azoxy Compounds by the Action of Phenyl Hydroxylamine on p-Nitroso-phenetol.

(a) Preparation of Phenyl Hydroxylamine.

Phenyl-hydroxylamine was prepared by the method as given by Gatterman¹⁵. A solution of ten grams of ammonium chloride in 320 grams of water was treated with 20 grams of freshly distilled nitrobenzene. In the course of an hour, 30 grams of zinc dust were added with continual stirring. The liquid was kept at about 13°. After all the zinc had been added it was stirred for ten minutes, then filtered with suction from the zinc oxide and after removing the filtrate, the residue washed with water. Both solutions were salted out with NaCl, cooled to 0°, and filtered with suction without washing. The yield obtained was 4.5 grams.

(b) Preparation of p-Nitroso-phenol.

p-Nitroso-phenol was prepared according to the method given by Bridge¹⁶. A mixture of 150 gms. of sulphuric acid and 400 c.c. of water at 70° was added to a solution of 60 gms. of

phenol, 27 gms. of sodium hydroxide and 54 gms. of sodium nitrite in 1500 c.c. of water. After the mixture had stood for two hours it was filtered, washed with ice water and extracted with ether. A yield of 45 gms. was obtained.

(c) Preparation of p-Nitroso-phenetol.

Following the directions as given by Hultman and Kamm¹⁷ p-nitroso-phenetol was made by adding gradually to 50 c.c. of absolute alcohol, 4 c.c. of concentrated sulphuric acid. This was cooled and 10 gms. of p-nitroso-phenol were added. After ten minutes the mixture was poured into water and extracted with ether. The ether extract was washed with dilute sodium hydroxide and then with water. After evaporating the ether, a yield of 5 gms. was obtained.

(d) Attempt to Prepare p-Ethoxyazoxybenzene.

Experiment 1.

1 gram of phenyl-hydroxylamine and 1.38 gms. of p-nitroso-phenetol were dissolved separately in the smallest amount of alcohol possible, the temperature being kept at about 0°. These amounts are molecular proportions. The solutions were mixed and allowed to stand surrounded by an ice bath for about ten hours. A light yellow crystalline precipitate was formed. This was filtered off with suction. The yield was 0.4 gms. The melting point was found to be 137° when the substance became milky, clearing up at 165°. After recrystallization from alcohol the melting point was practically unchanged. The filtrate was evaporated until about two thirds of the alcohol was gone. On cooling crystals separated out which melted after recrystallization at 136°, clearing at 167°.

both crops of crystals were p-azoxy phenetol.

Experiment 2.

3.9 gms. of phenyl-hydroxyl-amine and 5.44 gms. of p-nitroso-phenetol, molecular proportions, were mixed in a small flask without the aid of a solvent. A rather violent reaction took place. After cooling, a brown solid was formed and a rather strong odor of p-nitroso-phenetol was given off. On recrystallizing from alcohol, a yellow compound melting at $121-124^{\circ}$ was obtained. This was again recrystallized from alcohol and the light yellow crystals melted at 137° to a milky liquid which cleared at 167° . The product was again p-azoxy phenetol.

(e) Attempts to Prepare Ethoxyazobenzene.

Experiment 1.

5 gms. of p-nitroso-phenetol were mixed with 3.1 gms. of aniline and the mass melted together. No reaction occurred after ten minutes. The mixture was poured into water and the two substances separated as oils. The p-nitroso-phenetol was recovered by extracting with ether, washing with hydrochloric acid and evaporating the ether.

Experiment 2.

No reaction occurred when molecular amounts of aniline and p-nitroso-phenetol were mixed in ether solution. The p-nitroso-phenetol was recovered.

B. Preparation of an Unsymmetrical Azoxy Compound by the Reaction of a Mixture of Nitro Compounds with Sodium Hydroxide in Alcohol Solution.

(a) Preparation of α -Nitro-naphthalene.

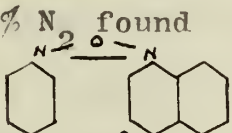
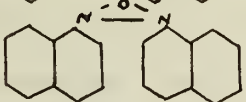
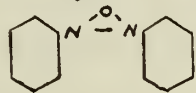
α -Nitro-naphthalene was prepared according to the method given by Jones¹⁸. 375 grams of nitric acid (sp. gr.1.33) were poured upon 75 gms. of naphthalene and the mixture allowed to stand twenty-four hours. Water was added to dilute the acid and the precipitate was collected and dried. Enough alcohol to moisten the product and sufficient carbon disulphide to dissolve it were then added. A small amount of dinitronaphthalene which was insoluble was filtered off. The carbon disulphide was distilled off and the nitro compound recrystallized from alcohol. 85.6 grams of crystals were obtained melting at 61°.

(b) Preparation of Phenyl-azoxynaphthalene.

The directions for making phenyl-azoxynaphthalene were adopted from the method of preparing azoxybenzene as given by Lachman¹⁹. To prepare methyl alcohol free from acetone, it was distilled from several grams of anhydrous sodium carbonate, the first 50 cc. containing most of the acetone. The alcohol was tested for acetone by treating 1 cc. diluted with 4 cc. of water with a mixture of 1 cc. of phenyl hydrazine and 3 cc. of dilute acetic acid. No precipitate was obtained.

To 200 cc. of purified methyl alcohol, 45 gms. of powdered commercial sodium hydroxide, 21.5 gms. of α nitro-naphthalene and 15.3 gms. of nitro-benzene (molecular amounts) were added. Heat was given off and the mixture turned dark brown. This mix-

ture was boiled on a water bath for three hours. Most of the alcohol was distilled off and the residue steam distilled to remove nitro-naphthalene and nitro-benzene. On pouring into cold water, a dark brown, sticky mass separated out but on crystallizing this from methyl alcohol a small amount of brown crystals was obtained M.P. 65-68°. On recrystallizing they melted at 67-68° and after another recrystallization the melting point remained constant. A determination of nitrogen was made.

Weight of substance	.1568 gms.
Cubic centimeters of N ₂	15.4 cc. at 736 mm. and 26°
% N ₂ found	10.62
% N ₂ in 	11.2
% N ₂ in 	9.3
% N ₂ in 	13.38

The substance was probably phenyl azoxynaphthalene, which has not previously been described in the literature.

C. The Preparation of an Unsymmetrical Azoxy Compound by Oxidation of the Azo Compound with Hydrogen Peroxide.

(a) The Preparation of p-Hydroxyazobenzene.

The directions for preparing p-hydroxyazobenzene were adopted from the directions given by Erdmann²⁰ for the preparation of ethyl dioxyazobenzene.

A solution of 226.5 grams of aniline and 570 cc. of 20% hydrochloric acid in 3300 cc. of cold water was diazotized with a sol-

ution of 105 gms. of sodium nitrite in 825 cc. of water. This solution was run into a solution of 156 gms. of phenol and 330 gms. of sodium carbonate in 600 cc. of water. After an hour, the p-hydroxyazobenzene was filtered off. A yield of 320 gms. of crude product was obtained.

(b) Preparation of Ethyl ether of p-Hydroxy-azobenzene.

Following the directions given by Jacobson and Fischer²¹ the ethyl ether of p-hydroxy-azobenzene or ethoxy azobenzene was prepared by heating 40 gms. of p-hydroxy-azobenzene with a solution of 5 gms. of sodium in alcohol and 35 gms. of ethyl iodide. The hydroxy-azobenzene was added first to the sodium ethylate and then ethyl iodide was added. The mixture was heated about three hours on a water bath. The solution was then poured into a large amount of water made alkaline with sodium hydroxide so that the unchanged p-hydroxy-azobenzene would stay in solution. The ether was recrystallized twice from alcohol, finally melting at 77-78°. A 15% yield was obtained. The melting point given in the theoretical is 77-78°.

An attempt was made to prepare this compound by heating the sodium salt of the hydroxyazobenzene with ethyl bromide in a sealed tube. 40 gms. of p-hydroxy-azobenzene was added to 4.64 gms. of sodium dissolved in absolute alcohol. The sodium salt did not separate out. The solution was evaporated down and a reddish brown tarry substance was obtained. Water and hydrochloric acid were added and the compound decomposed with gas with the formation of a tarry substance on top. The azo compound could not be extracted with ether. The hydroxy-azobenzene was probably mixed with diazonium compound which decomposed when the solution was heated.

To a solution of 40 gms. of p-hydroxy-azobenzene and 4.64 gms. of sodium in absolute alcohol, 22 gms. of ethyl bromide were added and the mixture was sealed in three glass tubes. It was intended to heat the mixture in an oil bath at 140° for six hours, but after the tubes have been heating for a half hour at 140° , one of them blew up. The other two were cooled and on standing at room temperature for two hours, they both blew up. Probably the diazonium compound present as impurity decomposed with the liberation of nitrogen.

(c) Preparation of Azoxybenzene.

Azoxybenzene was prepared by the method given by Angeli⁶. 3.11 grams of perhydrol (30% H_2O_2) were added to 5 grams of azobenzene in glacial acetic acid solution. The azobenzene separated out but went into solution again on the addition of more acetic acid. The solution was allowed to stand nine days and no change in color was observed. The solution was then divided into two portions and one part was heated under the reflux condenser on a water bath for about twenty minutes. The solution became light yellow indicating that reaction had taken place. Part of the solution was poured into water where a yellow oil separated. On extracting with ether and evaporating, light yellow crystals separated out. These were recrystallized from methyl alcohol. The crystals melted at 37° and were azoxybenzene.

(d) The Preparation of p-Ethoxyazoxybenzene.

In the same way, ethoxyazoxybenzene was prepared. 2.51 grams of perhydrol were added to a solution of 5 grams of ethyl ether of ^{ethoxy}p-azobenzene in glacial acetic acid. The solution was allowed to stand ten days, the liquid becoming slightly lighter

in color. The solution was heated to boiling on a reflux for about ten minutes, poured into water and extracted with ether. The ether was evaporated and the remaining crystals washed free from acetic acid with water. The crystals were again dissolved in ether and extracted with 5% sodium hydroxide. The sodium hydroxide extraction which was colored yellow was acidified and extracted with ether. After evaporating the ether, a small amount of dark brown crystals, probably phenol, was obtained. After drying on a clay plate and washing several times with alcohol, these crystals became lighter in color and melted at $57-60^{\circ}$. The main product in ether solution yielded orange-colored crystals which melted at $57-59^{\circ}$. By fractional crystallization they were separated into two portions. One fraction which consisted of yellow flaky crystals melted at $58-59^{\circ}$. These crystals were recrystallized until they showed a constant melting point.

Table of Melting Points.

1st. crystallization			$58-59^{\circ}$
2nd.	"	"	$57-59^{\circ}$
3rd.	"	"	$57-58^{\circ}$
4th.	"	"	$55-57^{\circ}$
5th.	"	"	$54-56^{\circ}$
6th.	"	"	$54-55^{\circ}$
7th.	"	"	$54-55^{\circ}$

The other portion which consisted of orange-colored needles, melted at $62-65^{\circ}$. This fraction was also recrystallized until constant melting points were obtained.

1st. crystallization		62-65 ⁰
2nd.	" "	63-67 ⁰
3rd.	" "	64-67 ⁰
4th.	" "	65-68 ⁰
5th.	" "	66-69 ⁰
6th.	" "	68-70 ⁰
7th.	" "	69-70 ⁰
8th.	" "	69-70 ⁰
9th.	" "	69-70 ⁰

In an attempt to determine if either fraction was a mixture two parts of the lower melting fraction were mixed with one part of ethoxyazobenzene. M.P. 52-58⁰. Then two parts of the higher melting fraction were mixed with one part of ethoxyazobenzene. M.P. 70-75⁰ and 71-76⁰.

Analysis of the Supposed Isomers of p-Ethoxyazoxybenzene.

Both products were dried on a clay plate over sulphuric acid in a vacuum and determination of nitrogen made.

Data.	Lower melting fraction -	M.P. 54-55 ⁰
	Weight of sample -	.1500
	c.c. of N ₂ obtained -	16. cc. at 741 mm. & 24 ⁰
	% N ₂ found -	11.67%
	Theoretical % N ₂ in ethoxyazoxybenzene-	11.57%

This compound is ethoxyazoxybenzene and its melting point agrees with that of one of the azoxy isomers isolated by Angeli.

Higher melting fraction	-	M.P. 69-70 ⁰
Weight of sample	-	.2000
cc. of N ₂ obtained	-	22.8 at 26 ⁰ and 741 mm.
% N ₂ obtained	-	12.46%
Theoretical % N ₂ in ethoxyazobenzene	-	12.39%
Theoretical % N ₂ in ethoxyazoxybenzene	-	11.57%

This fraction was probably a mixture of ethoxyazobenzene and ethoxyazoxybenzene. As only a small amount of the fraction was obtained the results from a series of combustions could not be obtained. Two compounds with melting points at 55⁰ and 72⁰ were reported by Angeli¹². The compound melting at 55⁰ corresponds to the one melting at 54-55⁰ obtained in this experiment. It is pointed out that perhaps the compound melting at 72⁰ obtained by Angeli is a mixture.

II.

Preparation of p-Aminophenol by Reduction of p-Hydroxyazobenzene with Iron.

By request of Dr. Stagner of the Mellon's Institute of Pittsburgh, Pa., p-aminophenol was prepared by the reduction of p-hydroxyazobenzene with iron. The method used is similar to that given in Friedlander²².

To 20 grams of powdered iron, 1 cc. of concentrated hydrochloric acid diluted with about 20 cc. of water was added. After stirring with an iron spatula, 20 gms. of p-hydroxyazobenzene were added with stirring and warming on a water bath. Enough water was added to keep a thick paste. Finally 50 cc. of HCl (1:1) were slowly added. Quite a strong reaction, probably the main one, took place here. Then an additional 40 cc. of concentrated hydrochloric acid were added, the solution warmed and then filtered. A rubber-like, black substance was left on the filter. As the p-aminophenol hydrochloride did not crystallize out on cooling, a piece of iron was added and the solution evaporated to about one-half the volume. On cooling, some crystals separated out. These consisted of a mixture of p-aminophenol hydrochloride, aniline chloride and iron salts. On washing these crystals with 1-3 hydrochloric acid in the cold, then treating with sodium carbonate and extracting with a little ether, aniline was first obtained. On extracting again with ether, p-aminophenol was obtained which softened at 180° and then finally melted at 187° . On recrystallizing, it melted at $183-184^{\circ}$.

Summary.

Three methods for the preparation of unsymmetrical azoxy compounds were investigated.

(1) An attempt was made to prepare unsymmetrical azoxy compounds by the action of a hydroxylamine on a nitroso compound. A mixture of the symmetrical azoxy compounds was obtained.

(2) An unsymmetrical azoxy compound, phenyl-azoxy-naphthalene was prepared by the reaction of sodium hydroxide upon a mixture of nitro compounds in alcohol solution. The small yield makes the process impracticable for the preparation of unsymmetrical azoxy compounds.

(3) p-Ethoxyazoxybenzene was prepared by the hydrogen peroxide oxidation as given by Angeli. Two compounds, agreeing in melting points to compounds which he prepared by another method, were obtained. An analysis showed the compound melting at 54-55° to be the unsymmetrical azoxyether. The other compound melting at 69-70° is probably a mixture of p-ethoxyazobenzene with a little p-ethoxyazoxybenzene. It is pointed out that perhaps the compound obtained by Angeli melting at 72° is a mixture. This would disprove some of Angeli's evidence in favor of the formula $R-\overset{\text{O}}{\underset{\text{O}}{\text{N}}}=\text{N}-R$ for the azoxy compounds.

p-Aminophenol was prepared from p-hydroxyazobenzene by means of the iron reduction method.

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